

LITVINENKO, L.G. [Lytvynenko, L.H.]

Effect of organic substances on the pigment concentration and
chlorophyllase activity in *Enteromorpha* at different temperatures.
Ukr. bot. zhur. 17 no.5:32-37 '60. (MIRA 13:12)

1. Institut botaniki AN USSR, otdel biokhimii rasteniy.
(Color of plants)
(Plants, Effect of organic compounds on)
(Plants, Effect of temperature on)

LITVINENKO, L.G.; VOLOVIK, O.I.

Effect of some forms of nitrogen on the productivity of *Scenedesmus quadricauda* (Turp.) Breb. Ukr. bot. zhur. 19 no.3:28-33 '62.
(MIRA 15:7)

1. Institut botaniki AN USSR, otdel khimii rasteniy.
(Algae--Cultures and culture media)
(Plants, Effect of nitrogen on)

LITVINENKO, L.G. [Lytvynenko, L.H.]

Effect of organic nutrition on photosynthesis in *Scenedesmus*
quadricauda (Turp.) Breb. Ukr.bot.zhur. 19 no.5:21-25 '62.
(MIRA 16:1)

1. Institut botaniki AN UkrSSR, otdel biokhimii rasteniy.
(Photosynthesis)
(Algae—Cultures and culture media)

LITVINENKO, L.G. [Lytvynenko, L.H.]

Organic nutrients of *Scenedesmus quadricauda* (Turp.) Breb. under various light conditions. Ukr. bot. zhur. 19 no.6:64-69 '62.
(MIRA 16:2)

1. Institut botaniki AN UkrSSR, otdel biokhimii rasteniy.
(Algae--Cultures and culture media) (Plants, Effect of light on)

LEBEDEV, S.I.; LITVINENKO, L.G.

Chlorophyll biosynthesis in red and infrared regions. Dokl. AN
SSSR 160 no.6:1427-1429 F '65.

(MIRA 18:2)

1. Ukrainakaya sel'skokhozyaystvennaya akademiya. Submitted June
17, 1964.

L 26557-66 EWT(1)/FCC GN

ACC NR: AP6016979

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AUTHOR: Litvinenko, L. I.

ORG: Hydrometeorological Scientific Research Center, Moscow (Gidrometeorologicheskoy nauchno-issledovatel'skiy tsentr SSSR)

TITLE: Zonal circulation in equatorial latitudes

SOURCE: Meteorologiya i gidrologiya, no. 3, 1966, 26-32

TOPIC TAGS: weather map, wind velocity, atmospheric current, atmospheric circulation, troposphere

ABSTRACT: Maps of the directions of the zonal components of wind velocity for January and July 1959 were constructed on the basis of daily maps of the pressure pattern in the equatorial and tropical zones in order to obtain a clear concept concerning the distribution of zonal currents in the upper troposphere and lower stratosphere of the low latitudes. The following conclusions were drawn for this period. 1. Westerly winds in the upper troposphere of the equatorial zone are observed far more frequently than is ordinarily believed. In January easterly winds at the 200-mb level represent only "inclusions" on the background of westerly winds. 2. The distribution of zonal components of wind velocity with height in the equatorial zone at different longitudes has a complex character and averaging can lead to extinction of important features of the regime of zonal circulation. 3. Zonal air currents in the lower troposphere for the most part are small and their average velocity is 1-4 m/sec, and in the upper troposphere -- 5-8 m/sec. 4.

Card 1/2

UDC: 551.513(213)

L 26557-66

ACC NR: AP6016979

The dissimilar regime of zonal circulation at different longitudes can be attributed not only to the difference of circulation processes, but also to a considerable degree to the difference of the underlying surface. Orig. art. has: 1 table and 2 figures. [JPRS]

SUB CODE: 04 / SUBM DATE: 29Jul65 / ORIG REF: 007 / OTH REF: 005

Card

2/2

LITVINENKO, L.I.

Air exchange between the northern and southern hemispheres, Meteor. i
gidrol. no.6:29-31 Je '65. (MIRA 18:5)

1. TSentral'nyy institut prognozov.

LITVINENKO, L.I.

Some characteristics of the tropopause in equatorial and tropical
zones. Trudy Sred.-Az. nauch.-issl. gidrometeor. no.23:93-98 '65.
(MIRA 19:2)

LITVINENKO, L.I.

Meridional circulation of the atmosphere in the equatorial
zone. Trudy TSIP no.144:35-46 '65. (MIRA 18:11)

LITVINENKO, L.I.

Some characteristics of circulation in the equatorial zone.
Trudy TSIP no.146:29-36 '65. (MIRA 18:9)

LITVINENKO, L. M.

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Synthesis of derivatives of diquinovosyl sulfones and sulfonates. II. N-Glucosides from diquinovosyl sulfones and 1,4-dianthrodiphenyl sulfone, also anthrodiphenyl sulfone, and some of their derivatives. M. Kh. Chigryan and L. M. Litvinenko (Dnepropetrovsk State Univ. 9/1961).

Di- α -D-glucopyranosyl 1,4-dianthrodiphenyl sulfone (I) was prepared from 1,4-dianthrodiphenyl sulfone (II) and α -D-glucose in 10% yield. $\text{C}_{28}\text{H}_{30}\text{O}_{10}$, mp. 100-101°C. $[\alpha]_D^{20} + 15.0^\circ$ (pyridine). This reduces Fehling's soln., although fairly slowly, and reacts slowly with ammoniacal AgNO_3 . Similar coupling of 1 mole I with excess (3.45 moles) p - $(\text{CH}_3\text{CO})_2\text{SO}_2\text{C}_6\text{H}_4\text{NH}_2$ gave 85% p - $(\text{CH}_3\text{CO})_2\text{SO}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH})_2$ (III), decomp. 100° (from MeOH-H₂O), $[\alpha]_D^{20} - 29.1^\circ$ (pyridine). With increase of the AcOH concn. in the condensation up to 4N the reaction yields a new substance; thus 0.4 g. I and 1 g. anthrodiphenyl sulfone boiled in 3 ml. abs. MeOH and 0.9 g. AcOH 1 hr. gave 14% $\text{SO}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH})_2$ (IV), decomp. 210-18°, $[\alpha]_D^{20} - 110^\circ$ (pyridine), which failed to yield a bisulfite complex. Reduction of IV in aq. alc. NaOH with H_2S at room temp. gave

the corresponding amine, decomp. 100-70° $[\alpha]_D^{20} - 12.9^\circ$ (pyridine), which with BiH in pyridine-abs. EtOH gave 60% $\text{SO}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH})_2$ (V), decomp. 100-70° $[\alpha]_D^{20} - 12.9^\circ$ (pyridine). The reaction of I with NH_3 in MeOH gave 28% $\text{SO}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH})_2$ (VI), decomp. 100-70° $[\alpha]_D^{20} - 12.9^\circ$ (pyridine). IV Synthesis of 1,1'-iminodiquinovosyl sulfone and sulfonates. M. Kh. Chigryan, L. M. Litvinenko, and E. G. Kozlovskii. Dokl. Akad. Nauk SSSR 1961, 161, 1040. Passage of dry NH_3 at 0° into 0.5 g. diquinovosyl sulfone in 4 ml. abs. MeOH storage of the mixt. 7 days at 0-6°, and diln. with dry H_2O gave a viscous liquid, which, taken up in H_2O and pptd. with abs. iso- PrOH , then evapd. in vacuo, gave 60% $\text{C}_{28}\text{H}_{30}\text{O}_{10}\text{NS}$, indicating the addn. of 1 NH_3 mole; the product was hygroscopic, sol. in H_2O with

basic reaction, reduced Fehling soln., and was quite stable in aq. soln. at room temp.; it is also formed in 33% yield if a little AcOH is added to the mixt. It appears to be 1,1'-iminodiquinovosyl sulfone, i.e., a substance with a cyclic structure with 10 members in the main ring. It shows $[\alpha]_D^{20} 43.3^\circ$ (H_2O). Similar treatment of diquinovosyl sulfoxide with NH_3 in MeOH contg. a little AcOH similarly gave 1,1'-iminodiquinovosyl sulfide, a solid, whose properties are similar to those of the above described sulfone, although it is less stable, $[\alpha]_D^{20} 72.3^\circ$ (H_2O).

G. M. Kozlovskii.

LITVINENKO L. M.

GLUZMAN, M.Kh.; LITBINENKO, L.M.; TOKAREVA, Ye.

Synthesis of derivatives of dichinovosylsulfone and sulfoxide. Part 4.
Synthesis of 1,1'-iminodichinovosylsulfone and sulfoxide. Ukr.khim.zhur.
18 no.2:194-196 '52. (MLRA 6:9)

1. Khar'kovskiy gosudarstvennyy universitet.
(Sulfones) (Sulfoxides)

Synthesis of derivatives of diquinovosyl sulfone and sulfonide. V. Acetodibromodiquinovosyl sulfone and sulfonide. M. Kh. Chizman and L. M. Litvinenko (State Univ., Kharkov), *Ukrain. Khim. Zhurn.* 18:316-19 (1952); cf. C.A. 46: 13034d. — Octaacetyl-diquinovosyl sulfone (2.2 g.) was dissolved with shaking and cooling in 25 ml. H₂O in AcOH (d. 1.04) over 1.5 hrs. and the soln. was kept at room temp. 3 hrs., then treated with cooling with 100 ml. ice-H₂O and filtered immediately; the thoroughly washed and dried

product, obtained in 85% yield, was $O_2S[CH_2CH(CHOAc)]_2$.

$CHBrO_2$, acetodibromodiquinovosyl sulfone, m. 106-10° (from EtOH), $[\alpha]_D^{25} 102^\circ$ (CHCl₃). This (0.3 g.) and (0.3 g.) $p\text{-H}_2NC_6H_4SO_2C_6H_4NO_2$ in 3 ml. CH_2Cl_2 were refluxed 60 min. (heating has to be stopped when darkening begins), cooled rapidly, and treated with 6 ml. dry Et₂O and 6 ml. dry petr. ether; the viscous ppt. was washed with more dry Et₂O, yielding 60% corresponding *N*-glycoside, $C_{24}H_{28}O_{10}S_2$, powder, $[\alpha]_D^{25} 15.6^\circ$ (pyridine). Similarly octaacetyl-diquinovosyl sulfonide gave the acetodibromo deriv., $C_{24}H_{28}O_{10}S_2Br_2$, powder (from EtOAc), $[\alpha]_D^{25} 239^\circ$ (CHCl₃), which

with *p*-amino-*p*'-nitrodiphenyl sulfone gave 45% corresponding *N*-glycoside, $C_{24}H_{28}O_{10}S_2N_4$, powder, $[\alpha]_D^{25} -3.6^\circ$. The formation of the glycoside does not proceed in CHCl₃ soln. I failed to condense with Ag salt of 6-methylthionuracil after long refluxing in xylene, PhNO₂ or tetrahydrofuran.

VI. Structure of *N*-glucosides of diquinovosyl sulfone. R. I. 320-8. — *N*-Glucosides of diquinovosyl sulfone (I) have tri-

cyclic structure, essentially $O_2S[CH_2CH(CHOAc)]_2CH_2O$ or NR. The condensation products of the sulfone with *p*,*p*'-thi-aminodiphenyl sulfone (II) or the nitro-amino analog (III) have the structure of azonethine dyes: $SO_2[CH_2CH(OH)]_2CH:NC_6H_4(SO_2C_6H_4NO_2 - p - p)_2$ or $SO_2[CH_2CH(OH)]_2CH:NC_6H_4(SO_2 - p, p')$. The glucoside from I and III heated in pyridine with Ac₂O 30-40 min. gave the *hexa*-Ac deriv., decomp. 172-4°, $[\alpha]_D^{25} 8.2^\circ$ (Me₂CO). The deac. of Ac groups in this and similar substances is readily done by treatment of the substance in pure Me₂CO with 0.6N KOH in MeOH; the deacetylated glucoside ppts. immediately; the excess alkali is back-titrated. The condensation product of I with 2 moles II treated with Ac₂O-pyridine 2 days at room temp. gave 55% acetylated deriv., $C_{48}H_{56}O_{12}S_4$, m. 285°, $[\alpha]_D^{25} -80^\circ$ (pyridine). G. M. Kosolapoff.

LITVINENKO L.M.

GLUZMAN, M.Kh.; LITBINENKO, L.M.

Synthesis of derivatives of dichinovylylsulfone and sulfoxide. Part 6.
Structure of *N*-glucosides of dichinovylylsulfone. Ukr.khim.zhur. 18 no.3:
320-326 '52. (MLRA 6:9)

1. Dnar'kovskiy gosudarstvennyy universitet. (Sulfones) (Glucosides)

LITVINENKO, L.M.

Importance of the research of V.I.Sorokin in the chemistry of carbohydrates. Ukr.khim.zhur. 19 no.3:337-340 '53. (MLRA 7:4)

1. Khar'kovskiy gosudarstvennyy universitet im. A.M.Gor'kogo, kafedra organicheskoy khimii.
(Sorokin, Vasilii Ivanovich, 1848-1919) (Carbohydrates)

Hydrolysis of I.

Catalytic vapor phase hydrolysis of symmetrical trichlorobenzene. L. M. Litvinova and V. G. Ostroverkhov. *Dokl. Akad. Nauk SSSR*, 1956, 127, 1014. *Trudy Nauch.-Issled. Inst. Khim. i Khim. Fiz.* No. 11, 211-20 (1954). *Referat. Ser. Khim.*, 1956, Abstr. No. 5741. Data is given on the vapor phase hydrolysis of sym-trichlorobenzene (I) in the presence of silica gel (II), II + 0.2% CuCl₂ + 3% Cu(III), II + 1.1% CuCl₂ (IV), II + 1% CuCl₂ + 10% MnCl₂ + 5% Cu (V), II + 1% CuCl₂ (VI), II + 1.5% Cu₂(PO₄)₃ (VII), II + 3.5% Cu₂(PO₄)₃ (VIII), II + 1.5% Mn₂PO₄ (IX), II + 2% Cu₂(PO₄)₃ (X), II + 4.5% Cu₂(PO₄)₃ (XI), II + 1% WO₃ (XII), II + 1% Cu₂(PO₄)₃ + 4.5% Ca₂(PO₄)₃ (XIII), also for chlorobenzene (XIV) in the presence of XIII and VI. The expts. are performed in a continuous system at atm. pressure at 400-500° with a great excess of H₂O vapor for I and with a wt. ratio of 1:1 for H₂O-XIV. The max. % of phenols, mainly 3,5-dichlorophenol (XV), from the hydrolysis of I is in the presence of II 0, II 0.88 (470-500°), IV 1.03 (490-500°), V 0.98 (540-50°), VI 1.09 (570-10°), VII 1.42 (540-50°), VIII 5.24 (400-50°), IX 0, X 1.38 (540-50°), XI 0.98 (550°), XII 0.09 (560°), XIII 0.09 (500°). The hydrolysis of XIV over XIII yields (510°) 11.83% phenol, and over 0.48% VI at 500°. In the presence of the most selective and active XIII during the hydrolysis of I, a mixt. of phenols is formed with about 30-60% XV. An important role during the reaction is assigned to the pyrolysis of I. The production of pure I is described. N. Vasilev

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LITVINENKO, L.M.

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✓ Steric hindrance and reactivity. I. Acetylation of amino derivatives of biphenyl. L. M. Litvinenko and A. P. Grekov. A. M. Gorkii State Univ., Kharkov, *Ukraine*. *Khim. Zvez.* 20, 104-201 (1971) (in Russian). — Kinetics of the reactions of PhNH₂, 4-amino-4'-nitrobiphenyl, and 4-amino-4'-nitro-2,2'-dimethylbiphenyl with p-O₂NC₆H₄COCl were studied. It was demonstrated that the presence of p- and 2'-methyl groups in the biphenyl molecule weakens interaction of nitro and amino groups in the 4,4'-positions. It has been hypothesized that internal rotation of the aromatic rings of the biphenyl molecule about the intermolecular bond, and the noncoplanar structure of this molecule, account for the characteristic reactivity of amino derivatives of biphenyl in contrast to the analogous benzene derivatives. Clayton F. Holoway.

100-201

Liberman, L. M.

480

Reaction rates and reactivity of 2,2'-derivatives of 4-amino-4'-nitrophenyl. L. M. Liberman, Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1951, 800-71. Acylation of several aromatic amines and alcohols shows that the groups in 2,2'-positions greatly weaken the reactivity of nitro and amino groups with each other in p,p' -positions, by prevention of free rotation. The following values of rates of reaction of indicated acyl chlorides (BzCl , p -nitrobenzoyl chloride, AcCl , resp.) with the amines were found (k_1 , k_2 , k_3 , AS, shown, resp.): PhNH_2 : 0.075, —, 735, —; 0.611, —, 6900, —; 1.10, —, —, —. $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$: 0.0000421, —, 11810, —; 0.000097, —, 10400, —; 0.01149, —, —, —. $p\text{-PhC}_6\text{H}_4\text{NH}_2$: 0.00, 0.140, 6500, —; 0.53, 1.11, 6000, —; 43, 1.05, 2.22, 5700, —; 41.5, $p\text{-O}_2\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{NH}_2$: 0.0122, 0.007, 6200, —; 48.7, 0.053, 0.118, 6300, —; 44.7, 0.112, 0.8, 7700, —; 39.3, 2.43, $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3(\text{NH}_2)_2$: 4.2, 0.026, 0.101, 8100, —; 40.1, 1.14, 0.39, 6300, —; 33.6, 0.326, 1.77, 12600, —; 20.4. G. M. Kosolapov

PM 6/25/51

LITVINENKO, L.M.

Micromethod for determination of primary aromatic amines by potentiometric titration with sodium nitrite.
L. M. Litvinenko and A. P. Grekov (A. M. Gor'kiy State Univ., Kharkov). *Zhur. Anal. Khim.* 10, 164-8; *J. Anal. Chem. U.S.S.R.* 10, 163-6 (1955) (Eng. translation).—Dissolve 0.01-0.06 millimol. of the amine in 5-20 ml. 2-10% HCl. If the amine is insol. in HCl dissolve it in AcOH or CHCl₃ and then add HCl to approx. 2-10%. Add KBr (acts as diazotization catalyst) to make the soln. 0.3-0.4N with respect to it. Titrate the soln. with 0.01N NaNO₂ delivered from a microburet. The equivalent point is at the max. jump in potential $\Delta E/\Delta v$. The results are calcd. from % amine = $7.100/b$ where a is the number of ml. of NaNO₂ used, T is the titer of the NaNO₂ standardized against an amine, and b is the wt. of the sample. This procedure worked equally well in HCl concns. of 2-20% and in the presence of 10-80% AcOH or HCOOH. The method was applied to detn. of sulfanilic acid, aniline, *p*-nitroaniline, *m*-nitroaniline, 4-aminobiphenyl, 4-amino-4'-nitro-2,2'-dichlorobiphenyl, and benzidine. M. Hosen

① 7/97

Litvenenko, L. M.

8000

1060. Micro-method of determining primary aromatic amines by potentiometric titration with sodium nitrite. L. M. Litvenenko and A. P. Grikov (A. M. Gorki Kharkov State Univ.). Zh. Anal. Khim., USSR, 1960, 15 (6), 164-168. The method is based on the use of KBr as a catalyst. The amine (0.01 to 0.05 millimole) is dissolved in 5 to 20 ml of 2 to 10 per cent. HCl soln. With difficultly soluble amines the sample is first dissolved in acetic or formic acid and then treated with HCl to give a concn. of 2 to 10 per cent. Sufficient KBr to give a 0.2 to 0.4 N soln. is then added and the soln. is titrated, during energetic stirring, with 0.01 N NaNO_2 from a micro-burette, with platinum and quinhydrone electrodes. An accuracy of ± 1 per cent. is attainable. G. S. SMITH

Chen

PM: 1222

LITVINENKO, L. M.

USSR/ Chemistry - Organic Chemistry

Card 1/1 Pub. 116 - 11/25

Authors : Litvinenko, L. M., Grekov, A. P.

Title : The reaction kinetics of acylation of aromatic amines with acid chlorides

Periodical : Ukr. khim. zhur. 21/1, 66-70, 1955

Abstract : Three methods of controlling the reaction kinetics of aromatic amines with acid chlorides were tested for the purpose of selecting one suitable for the study of the kinetics of aromatic amine acylation in anhydrous solvents. The deficiencies of the A and B methods and the advantages of the C (most suitable) method are described. Some results obtained by all three methods are tabulated. Six references 3 USSR, 2 USA and 1 German (1933-1954). Tables.

Institution : The A.M.Gorkiy State University, Faculty of Org. Chemistry, Kharkov

Submitted : March 1, 1954

LITVINENKO, L. M.

USER/ Chemistry - Organic chemistry

Card 1/1 Pub. 116 - 11/30

Authors : Tsukerman, S. V.; Litvinenko, L. M.; and Grekov, A. P.

Title : Synthesis of methyl ethers of 4-amino- and 4-amino-4'-nitrodiphenic acid

Periodical : Ukr. khim. zhur. 21/3, 341-343, June 1955

Abstract : The synthesis of hitherto unknown methyl ether of 4-amino-4'-nitrodiphenic acid (methyl-4-amino-4'-nitrodiphenate) was accomplished through partial reduction of 4,4'-dinitrodiphenic acid with a methanol-water solution of sodium disulfide and esterification of the product obtained with methyl alcohol in presence of hydrogen chloride. It is shown that the melting point of methyl m-aminobenzoate is 53-54° which is much higher than the value known so far. Ten references: 5 German, 1 English and 4 USSR (1903-1955).

Institution : The A. M. Gorkiy State Univ., Faculty of Organ. Chem., Karkov

Submitted : November 12, 1954

LITVINENKO, L.M.; GREKOV, A.P.; TSUKERMAN, S.V.

Spatial structure and reactivity. Part 3. Restricted inner rotation and kinetics of the acylation of 2,2'-carbomethoxyl derivatives of 4-aminebiphenyl and 4-amine-4'-nitrobiphenyl. Ukr. khim.shur. 21 no.4:510-517 '55. (MLRA 9:2)

1.Khar'kovskiy gosudarstvennyy universitet, kafedra organicheskoy khimii. (Acylation) (Biphenyl)

LITVINENKO, L. M.

USSR/Chemistry - Organic chemistry

Card 1/1

Pub. 22 - 19/51

Authors

Litvinenko, L. M.; Tsukerman, S. V.; and Grekov, A. P.

Title

Retarded internal rotation and the reactivity of amino derivatives of biphenyl.

Periodical

Dok. AN SSSR 101/2, 265-268, Mar 11, 1955

Abstract

A study of the acylation reaction kinetics of biphenyl amino derivatives showed that the reaction between the NO_2 and NH_2 groups oriented in 4,4'-positions is considerably weakened if the internal rotation of the aromatic nuclei in the molecule is retarded by the introduction of 2,2'-alkyl substituents. The steric effect of 2,2'-carbomethoxyl groups on the reactivity of 4-amino-4'-nitrobiphenyl was investigated. The results obtained are described. Nine references: 3 USSR and 6 USA (1934-1954). Table.

Institution :

The A. M. Gorkiy State University, Kharkov

Presented by:

Academician I. N. Nazarov, November 2, 1954

LITVINENKO. 12

7
The potentiometric titration of hydrazides of carboxylic acids and their condensation products with hydrazine with sodium phthalate. M. Litvinenko, G. G. Zakharenko, and V. I. Kuznetsov, Gorki Kharkov State Univ., Ukr. Khim. Zh., 1967, 13, 141, 517-130; Ref. Zhur., Khim., 1967, Abstr. No. 15,624. An earlier method for the determination of aromatic amines by potentiometric titration with NaNO_2 in acid medium in the presence of KBr (Zhuk. Abstr., 1955, 2, 1069) is used. Dissolve the sample (≈ 0.25 millimole) in glacial acetic acid (1.5 ml), and make up to 25 ml with conc. HCl . Take a 5-ml aliquot (≈ 1 to 15 mg of substance), add ≈ 0.5 g of solid KBr , insert a platinum electrode and titrate with 0.01 N NaNO_2 with vigorous mechanical stirring. The end-point is determined by the max. increase of potential ($\Delta E/\Delta V$). About 20 hydrazides and their corresponding hydrazones have been analyzed by this method. The accuracy is no lower than that of the analysis of aromatic amines, and in several cases is greater than the accuracy of the classical Dumas method for the determination of N.

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1. $\frac{1}{2} \sqrt{N} \ln K D, L M.$

Synthesis of some halogen-containing amines and nitro derivatives of aryls. ⁷ L. M. Gilyuz'ko, A. P. Grekov, N. N. Yerkha, et al., Izv. Akad. Nauk SSSR Khim. Zhur., 1968, No. 10, p. 2211 (1968).

Reaction of 2-chloro-4-nitrobenzidine (I) by chlorination with NCl_4/NH_3 in boiling HCl does not take place (cf. Flürscheim, C.A. 1, 885) as the 2,6-dichloro deriv. forms instead. The desired product was only formed as follows: to 40 g. 6-O₂C₂H₄NH₂ is added 1.2 l. H₂O and 200 ml. concd. HCl ; the mixt. heated until dissolved, chilled rapidly to room temp. and the resulting suspension chlorinated with stirring until 9–1 g. Cl_2 is added; the ppt. is sepd. and extd. from it with hot dil. HCl (1:1), in which the dichloro deriv. is insol. I forms in 50% yield (after cooling the ext.), m. 104°. This (6.8 g.) suspended at 8° in 480 ml. H₂O and 160 g. af. concd. H_2SO_4 is treated with 20 g. NaNO₂ in 80 g. H₂O at 8°, stirred 0.5 hr., filtered and added to 100 g. KI, 50 g. iodine and 100 ml. H₂O, then heated on a steam bath, freed of iodine with NaHSO₃, and washed with H₂O, yielding 84% 2-chloro-4-nitrodobenzene, m. 93–100° (from MeOH). This (25 g.) heated to 210° is treated over 40 min. with 25 g. powd. Cu (activated by iodine in Me₂CO), keeping the pump. under 220°; after heating 2 hrs. with stirring, the mass is extr. with hot MePh and the residue steam distd. The residm. is steam distl. with superheated steam, yielding 43.5% 4,4'-diniro-2,2'-di-chlorobiphenyl, m. 107° (from MeCH). This (6 g.) in 600 ml. MeOH at 40° is treated dropwise with 30 ml. $M \text{Na}_2\text{S}$.

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 $\frac{1}{3}$

Litvinenko, L.M., Grekov, A.P., Verkhovod, H.N.

solu. (240 g. NaOH and 32 g. S heated with 600 ml. H₂O and 260 ml. MeOH until dissolved, then dild. to 1 l. with H₂O) at 40°; after 10 min. the mixt. is acidified with HCl, the soln. is evapd. and the residue extd. with hot 1:1 HCl, yielding on cooling the ext. 68% 4-amine-4'-nitro-2,2'-dichlorobiphenyl-HCl (II), m. 204-6° (from aq. HCl); heated with NaOH it gave the free amine, a glassy solid (from aq. MeOH); the amine boiled with Na₂S₂ (excess) in MeOH yields 2,2'-dichlorobenzidine. II (3 g.) in a hot mixt. of 6 ml. concd. HCl and 16 ml. AcOH was chilled to 0°, treated with 0.25 g. NaNO₂ in 7.5 ml. H₂O, filtered, and added slowly to 12 g. NaH₂PO₄·H₂O in 12 ml. concd. HCl at 0°; after standing overnight the mixt. was made alk. with 10% NaOH, the oil sepd., washed with H₂O and extd. with MeOH (boiling), and the MeOH exts. were treated with ... and evapd. yielding 1.7 g. syrupy 4-nitro-2,2'-dichlorobiphenyl which (1.7 g.) in 17 ml. warm EtOH was treated with 1 ml. 100% NaOH, H₂O and a little Pancy Ni (vigorous reaction); after the reaction moderated.

another ml. NaOH, H₂O and Ni was added and the process was repeated until gas evolution ceased completely. The hot solu. was filtered, treated with C, evapd., dried in vacuo and extd. with petr. ether, and the ext. treated with dry HCl yielding 18% 4-amine-2,2'-dichlorobiphenyl-HCl, free amine m. 78-4° (from aq. MeOH); 4-amination of 27 g. 2,2'-dichlorobenzidine in 100 ml. MeOH, 100% NaOH, 430 g. H₂O at 5° with 13 g. NaNO₂ and 10 ml. 10% NaOH filtration and addn. to 22 g. acid ... 14 g. 81 ml. H₂O

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Litvinenko, L.M.; Grevin, A.P.; Verkhovod, N.H.

(M. H.), yielded after usual treatment 100% 3-bromo-4-nitro-2,6-dibromophenyl, m. 107° (from MeOH). This was treated with C₆H₆ as described above at 200-10° (the temp. is very critical, then extd. with hot MePh and the extd. steam dried. It is superheated steam up to 220°, 10° fractions being collected separately; the fraction collected in any 10° interval was not homogeneous and the combined products were again steam distd., collecting at 190-200° 7 g. 4,4'-dinitro-2,6-dibromobiphenyl, m. 123° (from MeOH). This (3.3 g.) in 380 ml. MeOH was treated with 15.2 ml. M. Na₂S₂O₄ in aq. MeOH (described above), refluxed 10 min., acidified and worked up as usual, yielding 70% 4-amino-4'-nitro-2,6-dibromobiphenyl, a glass; HCl salt, m. 220-2°. The latter (0.4 g.) in 1.6 ml. AcOH with 3-5 drops of pyridine treated at 0° with 0.9 g. NaNO₂ in 0.6 ml. conc. HCl, then worked up as usual, yielding 4-amino-4'-nitro-2,6-dibromobiphenyl, a glass; HCl salt, m. 220-2°. The latter (0.4 g.) in 1.6 ml. AcOH with 3-5 drops of pyridine treated at 0° with 0.9 g. NaNO₂ in 0.6 ml. conc. HCl, then worked up as usual, yielding 4-amino-4'-nitro-2,6-dibromobiphenyl, a glass; HCl salt, m. 220-2°.

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pm 3/3

mpe

LITVINENKO, L.M.

(Steric hindrance and reactivity. V. Hindered rotation and kinetics of acylation of 2,2'-halo derivatives of 4-aminobiphenyl and 4-amino-4'-nitrobiphenyl. L.M. Litvinenko and L.P. Gerasimov (State Univ., Kuznetsov). Zhur. Obshch. Khim. 26, 339-34 (1952); et. C.A. 49, 10836; 51, 8008. In acylation, in C_6H_5 soln., of aminobiphenyl with 2,2'-position of the halogen atoms and 4-position of the NH_2 group, it was shown that the halogens in this location cause steric hindrance to rotation of the rings and thus weaken the interaction of NO_2 and NH_2 groups in β -position to each other. The samples of the amine and the acyl chloride in C_6H_5 in 2:1 molar ratio were mixed in a thermostat, and after a period of 1:3 min. of $Et_3NH-C_6H_5$ was added to consume immediately the unreacted acyl chloride, methyl red in $AcOH$ added, 1:3 HCl added to acidify the mixt., the org. solvent removed, and the aq. residue after addn. of K_2CO_3 (cf. C.A. 49, 15840) analyzed for the aromatic amine with HNO_3 . For acylation with C_6H_5COCl the following kinetic data was obtained (k_1 , k_2 , E , P_2 , and ΔS given): 4-aminobiphenyl, 0.533, 1.11, 8600, 7.1×10^4 , -41.4; 4-amino-4'-nitrobiphenyl, 0.0305, 0.118, 8600, 3.8×10^4 , -44.7; 4-amino-2,2'-dichlorobiphenyl, 0.0184, 0.017, 7805, 6.7×10^4 , -43.1; 4-amino-4'-nitro-2,2'-dichlorobiphenyl, 0.00379, 0.00393, 8200, 11.2×10^4 , -42.1; m - $NO_2C_6H_4NH_2$, 0.0211, 0.0260, 8700, 5.3×10^4 , -39; 4-amino-2,2'-dibromobiphenyl, 0.0181, 0.0482, 7900, 5.7×10^4 , -43.4; 4-amino-4'-nitro-2,2'-dibromobiphenyl, 0.00297, 0.00329, 8700, 6.6×10^4 , -43.1; m - $BrC_6H_4NH_2$, 0.0129, 0.0578, 8300, 3.8×10^4 , -38.8; $PhNH_2$, 0.68. The steric effect P , taken as unity for biphenyl at 35° and 50°, is calculated to be 1.05 for the 2,2'-dichloro deriv. at 35° and 1.70 at 50°; with the 2,2'-dibromo deriv. at 35° and 1.73 and 1.90, resp. (cf. C.A. 50, 31335). O. M. K.

LITVINENKO, L.M.

LITVINENKO, A.P.

Title : Analysis of the Chloranhydride of Acetylsalicylic Acid.

Orig. Publ. Zhur. Obshch. Khim. 1957, No. 4, 42-43
 APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000930210019-6"

Abstract: The method consists of the mixing of the chloranhydride of acetylsalicylic acid solution (1) in C_6H_6 with a benzene solution of $C_6H_5NH_2$; the amount of $C_6H_5NH_2$ exceeds by ~3 times (in a mol. ratio) that of (1). The excess of $C_6H_5NH_2$ is backtitrated potentiometrically with a solution of $NaNO_2$ using a Pt indicator electrode. The presence of the N-phenylamide of acetylsalicylic acid in the mix-

Card 1/2

requires ≤ 30 minutes.

Card 2/2

LITVINENKO, L.N.; GREKOV, A.P.

Spatial structure and reactivity. Part 2: Retarded internal
rotation and acylation kinetics of certain biphenyl amino derivatives.
Uch.zap. KHGU 71:165-175 '56. (MLRA 10:8)
(Stereochemistry) (Acylation)
(Biphenylamine)

LITVINENKO, L.M.; POLYAKOV, V.P.; ORNKOV, A.P.; CHERNETSKAYA, A.M.

Analysis of aminoantipyrine in testing aminopyrine production.
Med.prom. 11 no.1:46-48 Ja '57. (MLRA 10:2)

1. Kafedra organicheskoy khimii Khar'kovskogo universiteta imeni
A.M.Gor'kogo i Tsentral'naya laboratoriya Khar'kovskogo khimiko-
farmatshevicheskogo zavoda "Krasnaya zvezda"
(PYRAMIDONE) (ANTIPYRINE)

LITVINENKO, I.M.; POLYAKOV, V.P.; GREKOV, A.P.; CHERNETSKAYA, A.M.

Analysis of acetylsalicylic acid chloride. Med.prom. 11 no.4:
12-43 Ap '57. (MLRA 10:6)

1. Khar'kovskiy gosudarstvennyy universitet imeni A.M.Gor'kogo
i Khar'kovskiy khimiko-farmatsevticheskiy zavod "Krasnay zvezda".
(CHLORIDES)

73-2-12/22

AUTHORS: Litvinenko, L.M., Tsukerman, S.V., Grekov, A.P. and
Slobodkina, E.A.

TITLE: Space structure and reactivity. IX: Hindered internal rotation and kinetics of the acylation of 2,2'-dicarboisopropoxylic derivatives of 4-aminobiphenyl and 4-amino-4'-nitrobiphenyl. (Prostranstvennoye stroeniye i reaktzionnaya sposobnost'. IX: Zatomozhennoye vnutrenneye vrashcheniye i kinetika atsilirovaniya 2,2'-dikarboizopropoksil'nykh proizvodnykh 4-aminobifenila i 4-amino-4'-nitrobifenila).

PERIODICAL: "Ukrainskiy Khimicheskiy Zhurnal" (Ukrainian Journal of Chemistry), Vol.23, No.2, March-April, 1957, pp.223-227 (USSR).

ABSTRACT: In an earlier communication it was shown that the interaction between the NO_2 and the NH_2 groups is considerably weakened in the second molecule by introducing the 2,2'-position of the carbomethoxyl groups (1). Further investigations have now been carried out to obtain data for determining the kinetics of the acylation reaction of amino-derivatives in a benzene solution, especially of dicarboisopropoxylic derivatives. The 4-amino-4'-nitro-2,2'-dicarboisopropoxybiphenyl and 4-amino-2,2'-dicarboiso-

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73-2-12/22

Space structure and reactivity. IX: Hindered internal rotation and kinetics of the acylation of 2,2'-dicarboisopropoxylic derivatives of 4-aminobiphenyl and 4-amino-4'-nitrobiphenyl. (Cont.)

propoxybiphenyl were synthesised and the kinetics of acylation by *n*-nitrobenzyl chloride in a benzene solution were investigated. Table 2 gives results at 25 C and 50 C for the first compound and Table 1 values for the second compound at the same temperatures. On comparing the velocities of acylation of the 2 compounds it can be seen that the carboisopropoxyl groups possess clearly defined electro-acceptor character as the velocity constant during the transition from one compound to the second compound decreases to half its value. Table 4 gives the values of the factors F (which was defined by the authors as the factor of space interlinking weakening. It shows the effect of weakening of the nitro-group on the amino-group by the molecular system of the biphenyl due to the spatial interaction of the 2,2'-substituents). These factors are for molecular systems of non-substituted biphenyl and its derivatives with ester-grouping in the 2,2'-position. Data given in Tables 3 and 4 show that the

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73-2-12/22

Space structure and reactivity. IX: Hindered internal rotation and kinetics of the acylation of 2,2'-dicarboisopropoxylic derivatives of 4-aminobiphenyl and 4-amino-4'-nitrobiphenyl. (Cont.)

carboisopropoxylic derivatives are closely related to their carbomethoxy-homologues for reasons of their kinetic characteristics and also the effects of the 2,2'-substituents.

There are 4 tables and 7 references, 6 of which are Slavic.

ASSOCIATION: Kharkov State University imeni A.M.Gor'ki,
Chair of Organic Chemistry (Khar'kovskiy Gosudarstvennyy
Universitet imeni A.M.Gor'kogo, Kafedra Organicheskoy
Khimii).

SUBMITTED: October 1, 1956.

AVAILABLE: Library of Congress
Card 3/3

AUTHORS: Litvinenko, L.M. and Grekov, A.P.

73-2-13/22

TITLE: Space structure and reactivity. X: Hindered internal rotation and kinetics of the acylation of 4-amino-1,1'-binaphtyl and 4-amino-4'-nitro-1,1'-binaphtyl. (Prostranstvennoye stroyeniye i reaktsionnaya sposobnost'. X: Zatomozhennoye vnutrenneye vrashcheniye i kinetika atsilirovaniya 4-amino-1,1'-binaftila i 4-amino-4'-nitro-1,1'-binaftila).

PERIODICAL: "Ukrainskiy Khimicheskiy Zhurnal" (Ukrainian Journal of Chemistry), Vol.23, No.2, March-April, 1957, pp.228-232 (USSR).

ABSTRACT: Previously published investigations on this subject are mentioned briefly (viz. previous abstract). Analogous experiments have now been carried out on the kinetics of acylation of the 2 above compounds. The synthesis and purification of the compounds, starting materials and intermediates is described in detail. The same method for measuring the velocity of acylation was used as in the previous experiments. (Viz. previous abstract). Data are tabulated in Tables 1 and 2. Table 3 summarises previously obtained data for the kinetics of acylation. It shows that the velocity of acylation of the aromatic amino-group

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73-2-13/22

Space structure and reactivity. X: Hindered internal rotation and kinetics of the acylation of 4-amino-1,1'-binaphtyl and 4-amino-4'-nitro-1,1'-binaphtyl. (Cont.)

linked to the binaphthyl residue, is considerably smaller than in the case of analogous biphenyl derivatives. Table 4 gives the F-factors for the molecular systems 1,1'-binaphthyl, unsubstituted biphenyl and its derivatives with substituents in the 2,2'-position. (For definition of F see previous abstract). The ultraviolet absorption spectra of three isomeric binaphtyls - 2,2'-binaphtyl, 1,2'- and 1,1'-binaphtyl it was shown that the effect of spatial hindrance is almost absent in the case of 2,2'-binaphtyl and shows a maximum for 1,1'-binaphtyl. The authors point out that the value for the activation entropy increases during the transition of 4-amino-4'-nitrobiphenyl to its binaphtyl analogue.

There are 4 tables and 14 references, 7 of which are Slavic.

ASSOCIATION: Kharkov State University imeni A.M.Gor'ki, Chair of Organic Chemistry (Khar'kovskiy Gosudarstvennyy Universitet imeni A.M.Gor'kogo, Kafedra Organicheskoy Khimii).

SUBMITTED: October 1, 1956.

AVAILABLE: Library of Congress

Card 2/2

~~KRASOVITSKIY, B.M.~~

KRASOVITSKIY, B.M.; LITVINENKO, L.M.; SEROVA, T.A.

LITVINENKO, L.M.

Effect of space factors on the properties of dyes containing a biphenyl nucleus. Part 9: Effect of spatial structure on the color of monoazodyes, derivatives of biphenyl, fluorene, and binaphthyl. Ukr.khim.zhur. 23 no.4:501-504 '57. (MIRA 10:10)

1.Khar'kovskiy gosudarstvennyy universitet im. A.M. Gor'kogo.
(Stereochemistry) (Azo dyes)

483

AUTHORS: Litvinenko, L. M., and Grekov, A. P.

TITLE: Spatial Structure and Reactivity. Part 6. Kinetics of Acylation of 2-Amino fluorene and 2-Amino-7-nitrofluorene (Prostranstvennoye stroyeniye i reaktsionnaya sposobnost'. VI. Kinetika atsilirovaniya 2-aminofluorena i 2-amino-7-nitrofluorena)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, No. 1, pp.234-239 (U.S.S.R.)

ABSTRACT: In order to establish the relation between spatial configuration and reactivity in bi-nuclear aromatic amino-nitro derivatives, comparative studies were made on the kinetics of acylation reaction for 4-aminobiphenyl and 4-amino-4'-nitrobiphenyl on one hand and derivatives of these amines containing various substitutes in 2,2'-positions on the other hand. It was shown that an increase in the angle between the surfaces of benzene rings during the change from 4-amino-4'-nitrobiphenyl to its 2,2'-derivatives is due to the steric hindrances between 2,2'-substituents leading to a considerable weakening of the reaction of the NO_2 - and NH_2 -groups oriented in 4,4'-positions of the molecules of the compounds indicated. It was found that the fluorene system being more planar

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Spatial Structure and Reactivity

than the biphenyl system is a much better transmitter of electronic effects of the substituents. Attention is called to the fact that 2-aminofluorene is similar by its kinetic parameters to its very close analogue 4-amino-2,2'-dimethylbiphenyl whereas 2-amino-7-nitrofluorene differs from its analogue - 4-amino-4'-nitro-2,2'-dimethylbiphenyl by its energy and activation entropy values. The kinetic acylation data for 2-amino-7-nitrofluorene are in many respects analogous to the kinetic data of 4-amino-4'-nitrobiphenyl, Four tables. There are 16 references, of which 10 are Slavic.

ASSOCIATION: The Khar'kov State University (Khar'kovskiy Gosudarstvennyy Universitet)

PRESENTED BY:

SUBMITTED: January 14, 1956

AVAILABLE:

Card 2/2

5
4E4j

Detailed discussion and reactivity. VII. Interaction of
separated atomic groupings according to data of kinetics of
the reaction of acylation of 4-aminodiphenyl ether and 4-
amino-4'-nitrodiphenyl ether. L. M. Litvinenko, R. S.
Cheshtov, and A. D. Gofman (State Univ., Kharkov).
Zhur. Obshch. Khim. 27, 758-55(1957); cf. C.A. 50,
1343g, 51, 1886c. In the diphenyl ether system despite
the separation of the rings by bridge O the conduction of elec-
tronic effects from ring to the other occurs readily, as readily
as in 1,4-phenylene. Condensation of p-O₂NC₆H₄Cl with PhOH in
presence of electrolytic powder. Cu activated with iodine
in the presence of alkali, with removal of residual starting
material by glacial distn. after completion of the reaction,
gave 4-O₂NC₆H₄OPh; this (10 g.) in 100 ml. hot MeOH
treated with 7 ml. 0.8% Na₂H₂O₂, followed by Raney Ni
added gradually (C.A. 51, 6093c), yielded 85% 4-H₂NC₆H₄
OPh (I) in 84-5°, purified through the HCl salt; the amine
m. 83-5° (from aq. MeOH). Heating 18 g. p-O₂NC₆H₄Cl
OK with 9 g. p-ClC₆H₄NO₂ and 0.5 g. powder Cu activated
with iodine to 115-50° and adding even 1 hr. in 5 g. Cu (1
portions in all) gave after 20 hrs. 45% 4-O₂NC₆H₄OPh, m.
142-3°, which (10 g.) in 120 ml. MeOH treated gradually
with 20 ml. 1M aq. Me₂CO soln. of NaOH over 10 min. then
refluxed 15 min. yielded after usual treatment 24% p-O₂
NC₆H₄OPh (II), m. 133-4° (from aq. MeOH).
The two anilines were studied as to rate of acylation with
p-O₂NC₆H₄COCl (cf. C.A. 51, 6706d). The rate const. for
I at 25° was 1.20, at 50° 2.69, E 5570 cal./mole. PZ 1.49 X
10⁴ /mole-sec., ΔS[‡] = -41.5 cal./deg. mole. For II the
rate const. at 25° was 0.102, at 50° 0.270, E 7600, PZ 3.4 X
10⁴, ΔS[‡] = -30.0.
G. M. Rosolovskii.

RM

LITVINENKO, L. M.

79-11-43/56

AUTHORS: Litvinenko, L. M., Grekov, A. P.
Shapoval, L. D.

TITLE: Synthesis of Some Amino- and Nitro-Derivatives of Diphenyl Which Have 2,2'-Dimetoxyl- and 3,3'-Dimethyl-Groups (Sintez nekotorykh amino- i nitroproizvodnykh bifenila, soderzhashchikh 2,2' - dimetoksil'nyye i 3,3' - dimetil'nyye gruppy).

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, Nr 11, pp. 3115-3122 (USSR)

ABSTRACT: For kinetic investigations performed in the laboratory 2,2'-dimetoxyl- and 3,3'-dimethyl-derivatives of 4-aminodiphenyl and 4-amino-4'-nitrodiphenyl had to be made available. It was found that the synthesis of the metoxyl-derivatives is most expediently to be realized according to scheme 1 (see formulae). The easily accessible o-tolidine served as starting product for the synthesis of the methyl derivatives. Their synthesis is represented by scheme 2 (see formulae). The following of the intermediate and end products produced were hitherto not described in publications: 4,4'-dinitro-2,2'-dimetoxydiphenyl, 4-amino-4'-nitro-2,2'-dimetoxydiphenyl, 4-amino-2,2'-

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Synthesis of Some Amino- and Nitro-Derivatives of Diphenyl Which Have 2,2'-Dimetoxyl- and 3,3'-Dimethyl-Groups 79-11-43/56

dimetoxydiphenyl, 4-amino -2,2-dimetoxydiphenyl, 4-nitro-3,3'-dimethyldiphenyl (and 4-amino-3,3'-dimethyldiphenyl). Thus new methods are suggested for the synthesis of a number of intermediate products which are necessary for the production of the given diphenyl derivatives and some already known methods are more precisely defined. There are 13 references, 9 of which are Slavic.

ASSOCIATION: Khar'kov State University (Khar'kovskiy gosudarstvennyy universitet).

SUBMITTED: November 9, 1956

AVAILABLE: Library of Congress

1. Diphenyl - Derivatives - Synthesis

Card 2/2

AUTHORS: Litvinenko, L. M., Grekov, A. P.

79-12-30/43

TITLE: Spacial Structure and Reactivity (Prostranstvennoye stroeniye i reaktivnaya sposobnost').
XI. Slowed Down Inner Rotation and the Acylation Kinetics of 2,2'-Dithyloxy- and 3,3'-Dimethyl Derivatives of 4-Aminodiphenyl and 4-Amino-4 Nitrodiphenyl (XI. Zatomozhennoye vnutrenneye vrashcheniye i kinetika atsilyrovaniya 2,2'-dimetoksil'nykh - i 3,3' - dimetil'nykh proizvodnykh 4 - aminobifenila i 4 - amino- 4' - nitro-bifenila).

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, Nr 12, pp. 3332-3338 (USSR).

ABSTRACT: In order to complete and further develop the conceptions put down by the authors in earlier works the present work mentions the results concerning the kinetics of the acylation of 2,2-dimethoxy- and 3,3-dimethyl derivatives with p-nitrobenzoylchloride in benzene solution. These derivatives are: 4-amino-2,2-dimethoxydiphenyl, 4-amino-3,3'-dimethyldiphenyl and 4-amino-4'-nitro-3,3' - dimethyldiphenyl. At the same time the kinetics of m-anisidine was investigated under the same conditions (see formulae). These investigations served the purpose of explaining the dependence of the spacial structure on the reactivity. The authors showed that the transfer of the electron interaction of the NO₂ and NH₂ groups (in the positions 4 and 4') to the mo-

Card 1/2

Spacial Structure and Reactivity.

79.12-30/43

XI. Slowed Down Inner Rotation and the Acylation Kinetics of 2,2'-Dimethyloxy- and 3,3'-Dimethyl Derivatives of 4-Aminodiphenyl and 4-Amino-4 Nitrodiphenyl.

lecular system of biphenyl becomes weaker with the introduction of 2,2'-dimethoxy substituents, which is caused by the spacial difficulties developing on this occasion as they cause the change of the geometric configuration of the biphenyl molecule. This is, however, not the case if in the place of the molecular system of the unsubstituted biphenyl there is that of the biphenyl with 3,3' substituents. The latter is explained by the fact that the 3,3' substituents do not cause any remarkable effect on the inner rotation of the benzene nuclei in the molecules of biphenyl and its derivatives. There are 7 tables, and 15 references, 9 of which are Slavic.

ASSOCIATION: Khar'kov State University (Khar'kovskiy gosudarstvennyy universitet).

SUBMITTED: November 9, 1956.

AVAILABLE: Library of Congress.

- Card 2/2
1. 2,2'-Dimethyloxy derivatives - Acylation
 2. 3,3'-Dimethyl derivatives - Acylation
 3. Molecular rotation - Analysis

LITVINENKO, L.M.

KRASOVSKIY, B.M.; LITVINENKO, L.M.

E.S. Khotinskii; on his 80th birthday. Ukr. khim. zhur. 24
no.1:134-135 '58.

(MIRA 11:4)

(Khotinskii, Evgenii Semenovich, 1867-)

50V/79-28-8-10/66

AUTHORS: Litvinenko, L. M., Levchenko, M. P., Andronov, . M.

TITLE: Synthesis of Several Nitro and Amino Derivatives of Tolane
(Sintez nekotorykh nitro- i aminoproizvodnykh tolana)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 3, pp.2046-2049(US: 8)

ABSTRACT: Several of the authors' experiments required 4-aminotolane (4-aminodiphenylacetylene) and the corresponding 4'-nitro derivative, but neither compound was described in the literature. A general scheme for synthesizing these compounds for the experiments was formulated (R=H or NO₂). As the starting material compound (I), R=H, the trans-4-stilbene, was used. The intermediate product in this synthesis scheme, the 4-nitrotolane, was also previously unknown. As an interesting synthetic peculiarity it was found that of all the substances tried for the reduction, Na₂S₂ (NH₄)₂S, H₂S in pyridine solution, hydrazine hydrate in the presence of a nickel catalyst, and others, only that suggested by Ruggli (Ruggli, Ref 1), phenylhydrazine, was found to be a valid reagent for reducing the 2,2"-dinitrotolane. The presence of

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SOV/79-28-8-10/66

Synthesis of Several Nitro and Amino Derivatives of Tolane

triple bonds in compounds (III) and (IV) was proved in the following manner: 4-aminotolane was deaminated, giving a tolane which was identical with the model prepared of this hydrocarbon. The 4-amino-4-nitrotolane was easily converted to the above-mentioned 4,4'-diaminotolane by further reduction. Thus 4-nitrotolane, 4-aminotolane, and 4-amino-4'-nitrotolane were synthesized in this experiment for the first time (further explanations are given in the experimental section). There are 9 references, 2 of which are Soviet.

ASSOCIATION: Khar'kovskiy gosudarstvennyy universitet
(Khar'kov State University)

SUBMITTED: June 28, 1957

Card 2/2

Litvinenko, L.M.

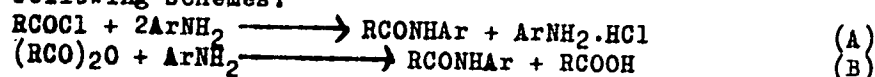
AUTHORS: Litvinenko, L. M., Aleksandrova, D. M.,

20-2-33/60

TITLE: The Influence of Acid-Admixtures on the Kinetics of the Acylation of an Aromatic Amine in an Inert Solvent (Vliyaniye kislotnykh dobavok na kinetiku reaktsii atsilirovaniya aromati-cheskogo amina v inertnom rastvoritele)

PERIODICAL: Doklady AN SSSR, 1958, Vol. 118, Nr. 2, pp. 321-324 (USSR)

ABSTRACT: This paper gives the results from the investigation of the influence of small admixtures of benzoic acid on the velocity of the reaction of the acylation of aniline by benzoylchloride and benzoic anhydride in benzoic acid. The experimental method has been described already in a previous work by the author (reference 1). The following was found: The acylation reaction of the aromatic amines by chlorine anhydrides and by anhydrides of the organic acids takes place according to the following schemes:



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If the acylation of aniline and its simplest derivatives by chlorine anhydride takes place in an inert solvent, the HCl-

The Influence of Acid-Admixtures on the Kinetics of the Acylation 20-2-33/60
of an Aromatic Amine in an Inert Solvent.

molecule, which was separated in the initial state of the reaction, immediately combines, according to the observations of various authors (references 6,7,8,9,10), with a second amine molecule, while a completely insoluble and, with regard to the acylating aniline is acylated by benzoyl-chloride and by benzoyl-chloride and by benzoin-anhydride the reaction velocity, under the influence of the admixtures of benzoic acid, increases remarkably. Benzoic acid is separated during the process of the acylation by benzoin anhydride. Therefore the reaction in pure benzene must be autocatalytic. The reason for the greatly different influence of hydrochloric acid and benzoic acid on the velocity of acylation according to the opinion of the authors, bases must likely upon the fact that these acids with the amine in the benzene solution come into interaction in various ways. For the reaction velocity in benzene containing benzoic acid an equation is written down. Between the velocity constant of acylation and the concentration of benzoic acid, a linear dependence is expected to be observed, which, however, has not been proved by the experiment. The reason for this fact might be the association of the carboxylic acids (Karbonovaya kislota) into with dimers. In the acylation of aniline by ben-

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The Influence of Acid-Admixtures on the Kinetics of the Acylation 20-2-33/60
of an Aromatic Amine in an Inert Solvent.

zoyle-chloride the temperature-dependence of the velocity-constant strictly obeys the equation by Arrhenius (Arrhenius), if the reaction takes place in pure benzene. The authors hope, after having ascertained some additional experimental data, to be able to report on the mechanism of the influence of acids upon the kinetics of acylation of aniline. There are 4 figures, 13 references, 6 of which are Slavic.

ASSOCIATION: State University imeni A. M. Gor'kiy, Khar'kov
(Khar'kovskiy gosudarstvennyy universitet im. A. M. Gor'kogo)

PRESENTED: August 16, 1957, by V. N. Kondrat'yev, Academician

SUBMITTED: July 30, 1957

AVAILABLE: Library of Congress

Card 3/3

AUTHORS: Litvinenko, L. M., Cheshko, R. S., Tsukerman, S. V. 20-118-5-27/59

TITLE: On the Interaction Between Separated Atomic Groups Through a System of Two Benzene Nuclei Connected by a Bridge (mostikovoye zveno) (O vzaimodeystvii udalennykh drug ot druga atomnykh gruppirovok cherez sistemu dvukh benzol'nykh yader, svyazannykh mostikovym zvenom)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 118, Nr 5, pp. 946-949 (USSR)

ABSTRACT: The mutual influence of atoms or atomic groups in complicated aromatic systems containing several benzene nuclei has only been investigated chemically in isolated and separated publications though a great amount of experimental material on this problem with regard to the simple benzene cycle is found. The authors proved for several amino derivatives of biphenyl that the interaction of the substituents through a system of 2 directly connected benzene nuclei is considerably weakened compared to the analogous benzene derivatives. Nevertheless it is still rather strong (reference 1 - 3). It was interesting to investi-

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On the Interaction Between Separated Atomic Groups
Through a System of Two Benzene Nuclei Connected by a
Bridge (mostikovoye zveno)

20-118-5-27/59

gate whether there is any interaction of substituents strongly different according to their nature (for instance of the NO_2 and NH_2 groups) at the opposite ends of the molecules, and if there is any, in what way it takes place. In this context not the previously investigated biphenyl derivatives are dealt with, but such compounds where the benzene cycles are not connected directly but are isolated from each other by a separating member. Though the interaction of the benzene cycles of the last-mentioned substances by a methylene bridge was stated (references 4 - 10) other authors maintained that the grey bridge of the aromatic sulfides must not be regarded as the agent of the conjugation (reference 13). The present paper is devoted to the chemical investigation of the problem mentioned above. The kinetics of the acylation reaction of 4-amino-diphenyloxide, 4-amino-4'-nitrophenyloxide, and of the corresponding sulfides by means of p-nitrobenzoylchloride in a benzene solution is described. The measuring methods for the velocity of this reaction were improved (compared to reference 14). The bimolecular velocity constants (k), the energy (E) and the entropy (ΔS) of the activation, and the frequency factor (PZ) were computed according to the methods described before (reference

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On the Interaction Between Separated Atomic Groups Through a System of Two Benzene Nuclei Connected by a Bridge (mostikovoye zveno) 20-118-5-27/59

ces 2,3). The numerical results for each investigated reaction are compiled in table 1. They show that contrary to the phenyl group which has a very weak electron absorbing power, the C_6H_5O group has rather a perceptible electron emission action. The analogous C_6H_5S group on the other hand has quite an electron absorbing nature, in spite of the fact that its introduction into the para position of the aniline molecule retards the acylation velocity almost by the fivefold. The authors propose a term "f" which would denote a relation of the velocity constants for reactions of the substituted and non-substituted compound. "f" shows how the reaction velocity is modified by the effect of the respective substituent on the reacting group. The comparison of the molecular systems of diphenyloxide and of diphenylsulfide surprisingly showed that the interaction of the substituents NO_2 and NH_2 at the transition from the biphenyl system to the systems of diphenyloxide and of the corresponding sulfide was not only not decreased, but in the case of the compound con-

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On the Interaction Between Separated Atomic Groups
Through a System of Two Benzene Nuclei Connected by a
Bridge (mostikovoye zveno)

20-118-5-27/59

taining O, was a little increased, and was perceptibly increased in the molecule of the diphenylsulfide derivate. Thus the O and S atoms do not act as insulators for electron effects if they push apart 2 benzene nuclei. At present the explanation is not easy. Frequently used methods of optical investigation often lead to contradictory results. These contradictions between the results of the chemical and the optical methods cannot be ascribed to any errors of these methods. This is only a pseudo-contradiction. All methods must be applied in this case.

There are 1 table, and 18 references, 11 of which are Soviet.

ASSOCIATION: Khar'kovskiy gosudarstvennyy universitet im. A. M. Gor'kogo
(State University imeni A. M. Gor'kiy, Khar'kov)

PRESENTED: October 8, 1957, by B. A. Kazanskiy, Academician.

SUBMITTED: December 1, 1956.

Card 4/4

24.7900

69961

SOV/141-2-4-16/19

AUTHORS: Tokar', S.Ye. and Litvinenko, L.N.

TITLE: Using the Paramagnetic Resonance Method for Determining the Concentration of Oxygen Dissolved in Water

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy, Radiofizika, 1959, Vol 2, Nr 4, pp 660 - 661 (USSR)

ABSTRACT: While studying paramagnetic resonance absorption in anthracite it had been noticed that the magnitude of the absorption fell sharply and then rose again when a pulverized sample was inserted in an evacuated enclosure. This was previously explained as due to paramagnetic atoms of atmospheric oxygen. The authors suggested that the effect could equally well be explained by the presence of oxygen dissolved in water adhering to the grains of coal. If this was so there should be an inverse proportionality between the total particle surface S of the coal and the intensity of absorption, Q (for a constant sample weight). Figure 1 shows this to be the case from measurements by Zavoy'skiy's method at $3 \cdot 10^8$ c/s. By outgassing the particles by boiling in distilled water

Card 1/2

LITVINENKO, L.M.; ALEKSANDROVA, D.M.; PILYUK, N.I.

Medium and reactivity. Part 1: Effect of additions of acid on the kinetics of the reaction between aromatic amines and benzoyl chloride in an inert solvent. Ukr.khim.zhur. 25 no.1:81-94 '59.

(MIRA 12:4)

1. Khar'kovskiy gosudarstvennyy universitet im. A.M. Hor'kogo, kafedra organicheskoy khimii.

(Amines) (Benzoyl chloride) (Chemical reaction, Rate of)

5 (3)
AUTHORS:

Litvinenko, L.M. and Levchenko, N.F.

SOV/79-29-3-36/61

TITLE:

Stereo Configuration and Reactivity (Prostranstvennoye stroyeniye i reaktsionnaya sposobnost')
XIII. Reaction of Atom Arrangements Distant From one Another According to the Investigation Data on the Kinetics of the Reaction of Amino Derivatives of Biphenyl and Stilbene, With *n*-Nitrobenzoyl Chloride and Picryl Chloride (XIII. O vzaimodeystvii udalennykh drug ot druga atomnykh gruppировок po dannym issledovaniya kinetiki reaktsii aminoproizvodnykh bifenila i stil'bena s *n*-nitrobenzoiikhloridom i pikrilkhloridom)

PERIODICAL:

Zhurnal obshchey khimii 1959, Vol. 29, Nr 3, pp. 924-935, (USSR)

ABSTRACT:

It is known that the substitution of the atoms -O- or -S- for the group -CH=CH- in the series of aromatic compounds does not eliminate their aromatic properties (Refs 4,5). In addition to earlier papers it seemed suitable to investigate the reactivity of such amines as (I) and (II), in which the bridging atom M (M=bridge) does not consist of -O- or -S- but of a vinylene arrangement, i.e. the reactivity of stilbene derivatives. According to references 6-10 it should be assumed that between the benzene nuclei in the molecular system of stilbene a considerably pronounced conjugation exists. No data, from the purely chemical aspect, were available on this problem in publications, although, especially in this respect,

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Steric Configuration and Reactivity

SOV/79-29-3-36/61

XIII. Reaction of Atom Arrangements Distant From one Another According to the Investigation Data on the Kinetics of the Reaction of Amino Derivatives of Biphenyl and Stilbene, With n-Nitrobenzoyl Chloride and Picryl Chloride

according to the previous investigations made by the authors (Refs 1,4) the chemical and optical methods of the investigation of such systems do not always yield clear results. The reaction kinetics of aniline, 4-aminobiphenyl, 4-amino-4'-nitrobiphenyl, 4-aminostilbene and 4-amino-4'-nitrostilbene with n-nitrobenzoyl- and picryl chloride in benzene solution was investigated. The molecular system of stilbene in which the benzene nuclei are separated by a bridge consisting of a vinylene arrangement was found to be a weaker conductor for the electronic influences (from one nucleus into the other) than the biphenyl system in which the benzene nuclei are directly linked with one another. The bridge vinylene arrangement between the benzene nuclei of stilbene transmits the electronic influence from one nucleus into the other far worse than the analogous oxygen and sulfur atom in the systems of the diphenyl oxide and -sulfide. There are 9 tables and 38 references, 24 of which are Soviet.

Card 2/3

Steric Configuration and Reactivity

SOV/79-29-3-36/61

XIII. Reaction of Atom Arrangements Distant From one Another According to the Investigation Data on the Kinetics of the Reaction of Amino Derivatives of Biphenyl and Stilbene, With n-Nitrobenzoyl Chloride and Picryl Chloride

ASSOCIATION: Khar'kovskiy gosudarstvennyy universitet
(Kharkov, State University)

SUBMITTED: November 22, 1957

Card 3/3

5(3)

AUTHORS:

Litvinenko, L. M., Levchenko, N. F.,
Tsukerman, S. V., Cheshko, R. S.

SOV/79-29-5-13/75

TITLE:

On the Reduction of Nitro Derivatives of Diphenyl Methane With Alkali Sulfides (K voprosu o vosstanovlenii nitroproizvodnykh difenilmetana sernistymi shchelochami)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1470-1474 (USSR)

ABSTRACT:

Recently the problem mentioned in the title was discussed in the dissertation of R. S. Tsekhanskiy (Ref 11). It was stated that 4-amino-4'-nitro-diphenyl-methane (I) with a melting point of 246° is formed by treating 4,4'-dinitro-diphenyl-methane with sodium sulfhydrate in aqueous alcohol solution. The authors found that not only (I) is formed there but also another substance with a melting point of 178° (II). Due to its bad solubility in alcohol it can be easily separated from the first substance. The investigation of the physical properties of (I) indicated that it is not 4-amino-4'-nitro-diphenyl-methane. It is of great importance for the clarification of the structure that 4,4'-diamino-diphenyl-methane can be transformed into 4,4'-diamino-benzophenone by treatment with alkali sulfides (Ref 18). It may be assumed that on interaction of the alkali

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On the Reduction of Nitro Derivatives of Diphenyl Methane SOV/79-29-5-13/75
With Alkali Sulfides

sulfide with 4,4'-dinitro-diphenyl-methane two processes take place: reduction of nitro groups to amino groups and transformation of the methyl groups to carbonyl groups. (I) really proved to be identical with the known 4,4'-diamino-benzophenone, which is obtained according to a method described in publications (Ref 21). 4,4'-diamino-benzophenone was found to be obtained more readily and in fair yield by treating 4,4'-dinitro-diphenyl methane with sodium disulfide in aqueous methanol. This method can be used as a new and convenient method for synthesizing this diamine. After the clarification of the structure of (I) it is no more difficult to confirm the structure of (II). By potentiometric titration with nitrite (II) was proved to be a monoamine. According to its melting temperature and other physical properties it is identical with 4-amino-4-nitro-benzophenone (Ref 22). Its definite structure was confirmed by its reduction with hydrazine hydrate in the presence of Reney nickel to 4,4'-diamino-benzophenone. By the influence of sodium disulfide upon 4-amino-diphenyl methane, also under more rigorous conditions than with the reduction of 4,4'-dinitro-diphenyl methane only 4-amino-diphenyl methane is obtained, i.e. no noticeable transformation of the methylene group into a carbonyl group takes place there. There are 24 references,

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On the Reduction of Nitro Derivatives of Diphenyl Methane SOV/79-29-5-13/75
With Alkali Sulfides

18 of which are Soviet.

ASSOCIATION: Khar'kovskiy gosudarstvennyy universitet (Khar'kov State University)

SUBMITTED: May 4, 1958

Card 3/3

(3)

SOV/79-29-8-62/81

AUTHORS:

Litvinenko, L. M., Levchenko, N. F., Krasovitskiy, B. M.,
~~Titarenko, N. I.~~

TITLE:

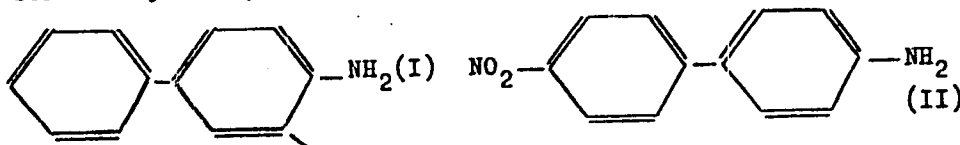
Spatial Structure and Reactivity. XIV. On the Interaction of the
Atom Groups Separated by One, Two, or Three Benzene Nuclei
According to the Investigation Data of the Reaction Kinetics of
Aromatic Amines With Picrylchloride

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 8, pp 2724-2729 (USSR)

ABSTRACT:

Recently Litvinenko and collaborators succeeded in determining,
during the investigation of the acylation kinetics of 4-amino-
biphenyl (I) and 4-amino-4-nitrobiphenyl (II) as well as aniline
and p-nitroaniline, that the effect of the nitro group upon the
reactivity of the aromatic amino group in the molecular system
of biphenyl is many hundreds of times weaker than it is in the
benzene system (Ref 1).



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Spatial Structure and Reactivity. XIV. On the Interaction of the Atom Groups Separated by One, Two, or Three Benzene Nuclei According to the Investigation Data of the Reaction Kinetics of Aromatic Amines With Picrylchloride

SOV/79-29-8-62/81

The ratio of the rate constants for the reactions of the amino and aminonitro derivatives may serve the quantitative evaluation

of this effect, e.g. $\frac{K_I}{K_{II}}$ (factor f)(Refs 2-5). In the present paper the authors dealt with the problem of how the effect of the NO_2 group upon the reactivity of the NH_2 group occurs when the same kinetic method is used in the case that these groups are separated from one another by a system of three benzene nuclei. The reaction of the aromatic amines with picryl chloride in a benzene solution was taken as an example, since it proved to be highly sensitive to structural changes in the amine molecule (Ref 6) and can therefore be successfully used for the quantitative characterization of the influence of the slightest differences in the structures of the named compounds upon the reactivity of the aromatically bound amino group. On the basis

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Spatial Structure and Reactivity. XIV. On the Interaction of the Atom Groups Separated by One, Two, or Three Benzene Nuclei According to the Investigation Data of the Reaction Kinetics of Aromatic Amines With Picrylchloride SOV/79-29-8-62/81

of these considerations the kinetics of the reaction of compounds (III) and (IV) with picryl chloride in benzene was investigated and compared to the data of the kinetics previously obtained for the reaction of picryl chloride with aniline-4-amino-biphenyl and 4-amino-4-nitrobiphenyl (Ref 7). It was shown that the nitro group has a very strong effect upon the reactivity of the amino group which occupies the para-position in the same benzene nucleus. This effect is reduced in the binuclear molecular system of biphenyl and disappears almost completely in the system of n-triphenyl. These phenomena are due to a specific structural spatial arrangement. There are 4 tables and 16 references, 14 of which are Soviet.

ASSOCIATION: Khar'kovskiy gosudarstvennyy universitet (Khar'kov State University)

SUBMITTED: July 10, 1958

Card 3/3

5(3)

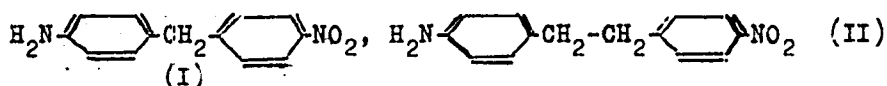
SOV/79-29-9-59/76

AUTHORS: Litvinenko, L. M., Levchenko, N. F.

TITLE: Synthesis of Some Nitro- and Amino Derivatives of Diphenyl Methane and 1,2-Diphenyl Ethane

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 3079-3082 (USSR)

ABSTRACT: The authors used 4-amino-4'-nitrodiphenyl methane (I) and the corresponding aminonitro derivative of 1,2-diphenyl ethane (dibenzyl) (II):



for investigations in their laboratory. Their task was to synthesize both compounds by partial reduction of the corresponding 4,4'-dinitro derivatives. The generally used alkali hydrosulfide lyes are unsuited in the present case since they cause undesired changes in the methylene groups of these compounds (Ref 1). Phenyl hydrazine proved to be a good reducing agent; compounds (I) with the melting point 98° and (II) (138°) resulted. The experience gained by the authors with

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SOV/79-29-9-59/76

Synthesis of Some Nitro- and Amino Derivatives of Diphenyl Methane and 1,2-Diphenyl Ethane

respect to the partial reduction of different aromatic dinitro compounds in which the nitro groups are in different and often not directly connected benzene rings, shows that phenyl hydrazine reacting with the nitro products according to the scheme $\text{ArNO}_2 + 3\text{C}_6\text{H}_5\text{NHNH}_2 \longrightarrow \text{ArNH}_2 + 3\text{C}_6\text{H}_6 + 2\text{H}_2\text{O} + 3\text{N}_2$ is one of the best and the most reliable acting agents for the partial reduction of the composite polynitro compounds. The reactions with phenyl hydrazine can be carried out the most conveniently in inert solvents (xylene, halogen derivatives of benzene, biphenyl etc). In difficultly reacting nitro compounds a high-boiling solvent must be used. Phenyl hydrazine is well suited as such (Ref 4). Also, the reduction with phenyl hydrazine is easy (see description in the experimental part). The structure of the products (I) and (II) was proved by their reduction into the known 4,4'-diamino derivatives of diphenyl methane and dibenzyl. Moreover, compound (II) was transformed by deamination into the known 4-nitrodibenzyl which in turn was reduced to the equally known 4-aminodibenzyl. The latter

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SOV/79-29-9-59/76

Synthesis of Some Nitro- and Amino Derivatives of Diphenyl Methane and 1,2-Diphenyl Ethane

synthesis of the rather difficultly accessible amino derivative of dibenzyl is of general preparative importance. There are 12 Soviet references.

ASSOCIATION: Khar'kovskiy gosudarstvennyy universitet (Khar'kov State University)

SUBMITTED: July 14, 1958

Card 3/3

53610

AUTHORS:

Litvinenko, L. M., Levchenko, N. F.69671
S/153/60/003/01/026/058
B011/B005

TITLE:

The Interaction of Substituents in Molecular Systems Consisting of Two Benzene Rings Connected by Hydrocarbon Bridges

PERIODICAL:

Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1960, Vol 3, Nr 1, pp 99-103 (USSR)

TEXT: The authors report in their paper on investigations of the kinetics of the reaction of 4-amino- and 4-amino-4'-nitro derivatives (I and IX) of di-phenylmethane, dibenzyl, trans-stilbene, tolane, and p-terphenyl with p-nitrobenzoyl chloride and picryl chloride in benzene solution. The methods were described already earlier (Refs 1-4). Table 1 shows the numerical results for each reaction and the results of other reactions investigated before. By a comparison of the ratios of the velocity constants of reactions of mono- and disubstituted derivatives (K_I/K_{II} - factor f) it is shown how the interaction of substituents is passed over from one benzene ring to the other. Table 2 shows the values of the factor f. These values show that the effect of the nitro group which in benzene very much reduces the reactivity of the amino group is considerably weakened if both groups are separated by benzene rings (biphenyl), and becomes very small if they are separated by 3 rings (p-

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69671

S/153/60/003/01/026/058

B011/B005

The Interaction of Substituents in Molecular Systems
Consisting of Two Benzene Rings Connected by
Hydrocarbon Bridges

terphenyl). This fact is explained by a reduced conductivity due to a greater distance and to the fact that the planes of the directly linked benzene rings must have a non-coplanar steric configuration. The introduction of a methylene bridge between benzene rings considerably reduces the value f in the molecular system of biphenyl. CH_2 acts here as an insulator reducing the interaction of benzene rings. Inductive effects, however, are intensively passed on by the methyl group. Two methyl groups effect a further reduction of the electron influence passing over from one benzene ring to the other. The f -values increase, however, by a separation of benzene rings in biphenyl by bridge atoms of oxygen or sulfur. In systems in which benzene rings are connected by 2-membered bridge groups, the conveyance of the electron influences increases only slightly by transition from the saturated ethane group (in dibenzyl) to an unsaturated one (in stilbene). This is an example for the compensation of the rupture of a bond in a continuous conjugate system by reduction of the distance between the interacting substituents. In tolane, the bridge group is even less saturated than in stilbene. Although the steric structure of the bridge seems especially favorable for the interaction of the 4,4'-substituent, the tolane system

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The Interaction of Substituents in Molecular Systems
Consisting of Two Benzene Rings Connected by
Hydrocarbon Bridges

S/153/60/003/01/026/058
B011/B005

probably conveys the interaction of substituents even worse than stilbene. Thus, a separation of the groups NO_2 and NH_2 by a growing system of conjugate bonds leads to a rapid extinction of the action of the former group on the reactivity of the latter. On the basis of their investigations, the authors state that the known rule saying that in conjugate systems the influence of a substituent is passed over without noticeable attenuation is not confirmed by the examples studied by them. B. M. Krasovitskiy and N. I. Titarenko took part in the investigation. There are 2 tables and 16 references, 14 of which are Soviet.

ASSOCIATION: Khar'kovskiy gosudarstvennyy universitet im. A. M. Gor'kogo;
Kafedra organicheskoy khimii (Khar'kov State University imeni
A. M. Gor'kiy; Chair of Organic Chemistry)

SUBMITTED: February 27, 1959

Card 3/3

LITVINENKO, L.M.; ALEKSANDROVA, D.M.

Reactivity and the surrounding medium. Part 2: Effect of adding certain nitrophenols on the kinetics of the reaction between aniline and benzoyl chloride in benzene. Ukr.khim.zhur. 26 (MIRA 13:5) no.1:66-68 '60.

1. Khar'kovskiy gosudarstvennyy universitet imeni A.M. Gor'kogo, kafedra organicheskoy khimii.
(Phenol) (Aniline) (Benzoyl chloride)

LITVINENKO, L.M.; ALEKSANDROVA, D.M.; ZHILINSKAYA, A.A.

Medium and reactivity. Part 3: Kinetics of the reaction of benzoylation of aniline by benzoic anhydride in benzene - benzoic acid mixtures. Ukr. khim. zhur. 26 no.4:476-489 '60. (MIRA 13:9)

1. Khar'kovskiy gosudarstvennyy universitet im. A.M. Gor'kogo, kafedra organicheskoy khimii.
(Aniline) (Benzoylation)

LITVINENKO, L.M.; ALEKSANDROVA, D.M.

Medium and reactivity. Part 4: Kinetics of the reaction between aniline and picryl chloride in mixtures of benzene and carboxylic acids and of benzene and nitrophenol. Ukr. khim. zhur. 26 no.5: 621-625 '60. (MIRA 13:11)

1. Khar'kovskiy gosudarstvennyy universitet im.A.M.Gor'kogo.
(Aniline) (Picryl chloride)

COPY

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S/079/60/030/05/58/074
B005/B125

5.3610

AUTHORS:

Litvinenko, L. M., Levchenko, N. F.

TITLE:

Steric Structure and Reactivity. XVI. Kinetics of the Reactions of Amino Derivatives of Diphenyl Methane and of Dibenzyl With p-Nitro-benzoyl Chloride and Picryl Chloride

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 5, pp. 1673-1680

TEXT: The authors of the present report investigated the kinetics of the reactions of p-nitro-benzoyl chloride and picryl chloride with 4-amino-diphenyl methane, 4-amino-4'-nitro-diphenyl methane and the two analogous derivatives of dibenzyl. The production of the initial products and the method of the kinetic measurements are given in the experimental section. Table 1 shows the results of the kinetic measurements for the eight reactions studied. The reactions were investigated at 25° and at 50°. Table 2 shows the summarized results of earlier investigations (Refs. 1-3) and the results of the present paper. In these four papers systems of two benzene rings were investigated which were bound either directly or by a hydrocarbon bridge ($-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}=\text{CH}-$, $-\text{C}\equiv\text{C}-$). It was to be

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Steric Structure and Reactivity. XVI. Kinetics of S/079/60/030/05/58/074
the Reactions of Amino Derivatives of Diphenyl B005/B125
Methane and of Dibenzyl With p-Nitro-benzoyl Chloride
and Picryl Chloride

determined to what degree a substitute in one of the benzene nuclei effects the other benzene nuclei. The ratio f of the two rate constants of the reactions of the p-amino derivative and the p-amino-p'-nitro derivative with p-nitro-benzoyl chloride or with picryl chloride was chosen as a measure of the transfer of the influence in a determined system. The comparative studies showed that the methylene group of the diphenyl methane inhibits the transfer of the effects of a substitute from one benzene nucleus to the others. That is the case to an even greater extent when the two benzene nuclei are separated by two methylene groups, as is the case with dibenzyl. Table 3 shows the values of f for the reactions of nine different molecular systems with p-nitro-benzoyl chloride and with picryl chloride at 25°. V. F. Lavrushin and N. A. Valyashko (Refs. 4, 5), V. A. Izmail'skiy, G. V. Alekseyeva, and R. S. Tsekhanskiy (Refs. 6, 7) and Ye. N. Gur'yanova (Ref. 21) are mentioned in the present report. There are 3 tables and 23 references, 21 of which are Soviet. X

Card 2/3

Steric Structure and Reactivity. XVI. Kinetics
of the Reactions of Amino Derivatives of
Diphenyl Methane and of Dibenzyl With p-Nitro-
benzoyl Chloride and Picryl Chloride

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S/079/60/030/05/58/074
B005/B125

X

ASSOCIATION: Khar'kovskiy gosudarstvennyy universitet (Khar'kov State
University)

SUBMITTED: March 18, 1959

Card 3/3

LITVINENKO, L.M.; LEVCHENKO, N.F.

Spatial configuration and reactivity. Part 17: Interaction between atomic groups located at some distance from each other, as determined from data on the kinetics of reactions of diphenylamine and azobenzene amino derivatives with p-nitrobenzoyl chloride and picryl chloride. Zhur.ob.khim. 30 no.8:2704-2714 Ag '60. (MIRA 13:8)

1. Khar'kovskiy gosudarstvennyy universitet.
(Benzoyl chloride)
(Picryl chloride)
(Diphenylamine)
(Azobenzene)

86506

5.4300

1142, 1273, 1297

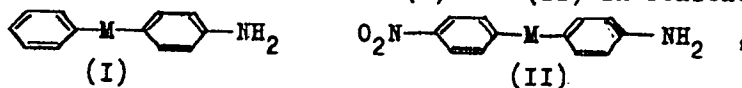
S/079/60/030/011/012/026
B001/B066

AUTHORS: Litvinenko, L. M. and Cheshko, R.S.

TITLE: Steric Configuration and Reactivity. XVIII. Reaction of Atom Groups Remote From One Another, According to Data Obtained for the Reaction Kinetics of Amino Derivatives of Diphenyl Oxide, Diphenyl Sulfide, and Diphenyl Selenide With Picryl Chloride

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 11, pp.3682-3692

TEXT: In the previous reports of this series (Refs.1-3), the investigation results of the reaction kinetics of p-nitro-benzoyl chloride with amino derivatives of the structure (I) and (II) in benzene were given



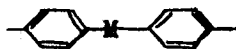
where M denotes the bridge atoms of oxygen or sulfur. It was shown that the influence of the nitro group upon the acylation rate of the amino group in the systems (III) becomes manifest with markedly greater inten-

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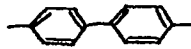
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Steric Configuration and Reactivity. XVIII. S/079/60/030/011/012/026
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 Another, According to Data Obtained for the Reaction Kinetics of Amino
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 With Picryl Chloride

sity than in the case of the diphenyl system (IV)



(III)



(IV)

(M = O or S),

which contains no separating bridge atom between the benzene nuclei. A quantitative characteristic of the capability of transmitting the interaction of the NO_2 and NH_2 groups in the molecular systems (III) and (IV) was the ratio of the rate constants in the reactions of the mono- and disubstituted derivative, e.g. K_I/K_{II} (factor f). The present report gives data on the investigation of the kinetics of similar reactions of amino derivatives of diphenyl oxide and diphenyl sulfide with picryl chloride, under equal conditions, which confirmed the kinetic results obtained in previous studies for the reaction which is particularly sensitive with respect to structural changes in the molecules of aromatic amino derivatives (Ref.4). In the molecular systems of diphenyl oxide,

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Steric Configuration and Reactivity. XVIII. S/079/60/030/011/012/026
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 With Picryl Chloride

diphenyl sulfide, and diphenyl selenide, in which the benzene rings are
 connected by means of the heteroatoms O, S, and Se, the 4'-NO₂ group
 affects the reactivity of the 4-NH₂ group in a distinctly higher degree
 than in the diphenyl system where the benzene nuclei are directly
 connected with each other. This fact confirms the higher intensity of
 electron transfer effects of substituents from one benzene ring into the
 other in systems which have bridges of heteroatoms. Student X
 V. M. Zikranets assisted in conducting the synthesis. There are 8 tables
 and 26 references: 17 Soviet, 4 US, 2 British, 1 Italian, and 1 French.

ASSOCIATION: Khar'kovskiy gosudarstvennyy universitet imeni
 A. M. Gor'kogo (Khar'kov State University imeni A.M.Gor'kiy)

SUBMITTED: January 1, 1960

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LITVINENKO, L. M.

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LITVINENKO, L.M.; ALEKSANDROVA, D.M.

Medium and reactivity. Part 7: Kinetics of the reaction of aromatic amines with benzoyl chloride in mixtures of benzene and acetic acid. Ukr. khim. zhur. 27 no.4:487-494 '61. (MIRA 14:7)

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(Amines) (Benzoyl chloride)

LITVINENKO, L.M.; ALEKSANDROVA, D.M.; PROKOPOVICH, S.F.

Medium and reactivity. Part 8: Kinetics of the acylation of aromatic amines with acetic anhydride and benzoyl chloride in benzene with chloracetic acid additions. Ukr. khim. zhur. 27 no.4:494-502 '61. (MIRA 14:7)

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(Amines) (Acylation)

LITVINENKO, L.M.; ALEKSANDROVA, D.M.

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LITVINENKO, L.M.; LEVCHENKO, E.F.

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